



PATENT SPECIFICATION

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DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in and relating to the concentrating of hydrogen.

We UNIVERSAL OIL PRODUCTS COMPANY, a Corporation organised under the Laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to the production of a gas stream of increased hydrogen concentration from a hydrogen-containing mixture of gases which involves the diffusion of hydrogen from the gas mixture through a hydrogen-permeable membrane. More specifically, the invention relates to a method and an apparatus for separating hydrogen in a high state of purity.

It is well-known that metals of Group VIII of the Periodic Table are permeable to hydrogen and substantially impermeable to other gases which may be mixed therewith in the commonly found gas mixtures containing hydrogen. Relatively thin membranes of such metals have heretofore been utilized in suitable equipment to effect at a relatively low rate the separation of hydrogen from other diverse gases. However, it has been found that the use of such thin metallic membranes, such as palladium foil, for this method of separation are limited in their application to low pressures and low rates of hydrogen production because of the tendency of such thin membranes to rupture upon the application of even slight pressures on the upstream side of the hydrogen-permeable foil.

Although palladium has been found to be one of the preferred hydrogen-permeable elements from which to fabricate such gas diffusion elements,

other metals of Group VIII of the Periodic Table such as iron, nickel, and platinum and also certain alloys of the latter metals, as well as alloys of a metal of this group with copper, silver, gold or molybdenum may be employed in the fabrication of a hydrogen-permeable membrane without sacrificing purity of the gaseous product obtainable by the use thereof, and without weakening the structural properties of the membrane. Thus, silver-palladium alloys containing from small amounts up to about 60 atom % of silver, and more particularly from about 25 to 40 atom per cent of gold, and boron-palladium the permeation rate of hydrogen through the membrane under otherwise similar conditions. Gold-palladium alloys, particularly those containing from 20 to about 40 per cent of gold, and boron-palladium alloys, more particularly those containing from small amounts up to 10 atom per cent of boron also increase the permeability of the membrane to hydrogen.

In order to provide a membrane which will permit a reasonable throughput rate of the hydrogen-containing gas mixture and thereby permit the production of hydrogen at a reasonable rate, the resistance to flow of hydrogen through the membrane may be reduced by providing a sufficiently thin foil; alternatively, higher upstream pressures may be utilized to increase the rate of diffusion of hydrogen through the permeable membrane, but accompanying such use of higher pressures is the necessity of providing a membrane of sufficient thickness to withstand the higher pressures, without rupturing the membrane. It has been found, however, that the rate of increase in the resistance to flow of hydrogen through the hydrogen-permeable membrane as the thickness of the membrane increases is greater than the rate of

increase in flow through the membrane with increases in pressure to the rupture point. Therefore, an increase in the thickness of the membrane to accommodate higher pressures defeats the purpose of higher pressures. The known processes employing hydrogen-permeable metal foils, for all practical purposes, are thus limited to low-pressures and to low rates of hydrogen production.

One object of this invention is to provide a method for concentrating hydrogen in which a product stream of high purity is obtained at a high rate of production without the use of bulky or cumbersome equipment. Another object of the invention is to provide a simple apparatus suitable for carrying out this method effectively and permitting the use of high pressures and high throughput rates for the gaseous mixture without the necessity of frequent replacement of the hydrogen-permeable membrane.

The method according to this invention comprises passing a hydrogen-containing mixture of gases at an elevated pressure and temperature through a diffusion zone separated into an upstream portion and a downstream portion by a membrane as hereinafter defined comprising a hydrogen-permeable metal of Group VIII of the Periodic Table, said membrane being supported against the upstream pressure by a rigid porous matrix comprising compressed sintered steel particles, and collecting a gas stream of higher hydrogen concentration than that of said mixture on the downstream side of said matrix while a gas stream having a lower hydrogen concentration than that of said mixture is collected on the upstream side of said membrane.

In a more specific embodiment of the method according to the present invention pure hydrogen is separated from a hydrogen-containing gas mixture by passing said mixture at an elevated pressure and temperature through a diffusion zone separated into an upstream portion and a downstream portion by a membrane as hereinafter defined consisting of a metal selected from Group VIII of the Periodic Table and the hydrogen-permeable alloys of said Group VIII metal, said membrane being supported on its downstream side against the upstream pressure by a rigid porous matrix produced from sintered steel particles of from 1 to 100 micron particle size, and collecting hydrogen on the downstream side of said matrix while a gas comprising the non-hydrogen component of said mixture is collected on the upstream side of said membrane.

This invention also comprises an apparatus suitable for effecting the concentrating or separation of hydrogen from a mixture of gases which comprises in combination a housing capable of confining a mixture of gases under pressure and at elevated temperature, a structurally rigid porous matrix which comprises compressed sintered steel particles and is sealed into the sides of said housing and between the ends thereof, a gas inlet to and a gas outlet from said housing on one side of said matrix, said inlet and outlet being spaced from each other, a separate gas outlet from the housing on the other side of said matrix, and a membrane as hereinafter defined which extends across the entire free area within said housing and is supported by said matrix, said membrane comprising a metal selected from Group VIII of the Periodic Table and the hydrogen-permeable alloys of said Group VIII metal.

The present invention permits the separation of hydrogen by gas diffusion at a relatively high pressure in conjunction with the use of a relatively thin membrane of the hydrogen-permeable metal, thereby combining the advantages of both high upstream pressures and thin hydrogen-permeable membranes for producing hydrogen at a high rate of production. This desirable result is achieved in the present invention by combining a relatively thin hydrogen-permeable membrane with the porous, structurally rigid support therefor which withstands the desired operating pressures applied to the upstream side of the membrane. The porous support for the membrane is a porous matrix composed of sintered particles of metal fabricated into a plate of substantial thickness capable of maintaining its structural rigidity in spite of high pressure differentials between the upstream and downstream sides of the membrane; the plate has sufficient surface area surrounding the open pores to support and maintain the continuity of the membrane at all points on the membrane exposed to the elevated pressure.

The porous matrix is generally manufactured by partially fusing a mass of the metal in powdered or finely divided condition, and compressing the heated mass of metal particles. Thus, a plate fabricated from powdered iron may be formed by compressing a mass of iron particles retained within a walled enclosure at a temperature near the melting point of the iron, the particles generally being compressed in a hydraulic press capable of exerting pressures of from 350 to about 7,000 kg/cm². The

steel particles from which the porous matrix for use in accordance with the present invention is to be fabricated may be supplied to the sintering press in a size range varying from finely powdered to coarsely pelleted form, individual particles of which may vary in size from 0.1 to 800 microns, preferably from 1.0 to 100 microns in diameter. The size of the steel particles in any event must be sufficient to produce a membrane-supporting plate having pores which will permit the free passage of molecular hydrogen through the pores of the resulting plate. Preferably, the porous matrix consists of compressed sintered stainless steel particles of from 1 to 100 micron particle size and has pores of not more than 100 micron diameter.

The porous matrix of compressed sintered steel particles provides a compressed plate of the greatest structural rigidity and strength retentiveness at the temperatures of use, the greatest resistance to warpage, the most readily controllable porosity and generally the greatest inertness to the hydrogen-containing gas stream to be separated. In fabricating a porous plate from powdered stainless steel heat may be applied, for example, by applying an electric current of high amperage to a mass of the powdered metal, fusion of the powdered particles taking place at the boundaries of each of the particles where the electrical resistance is the greatest and local temperatures attain the melting point of the metal. A plate manufactured of compressed sintered stainless steel powder may be utilized for the separation of corrosive gas mixtures such as mixtures of hydrogen and sulfur trioxide as well as for the separation of gas mixtures comprising hydrogen and low molecular weight hydrocarbon gases or hydrogen-nitrogen mixtures.

Any suitable method for fabricating a hydrogen-separation cell may be employed which will provide for collecting the diffused hydrogen component of the gas mixture in a separate zone from the non-diffused components of the mixture. The basic requirement in fabricating an apparatus for this purpose is the provision of a membrane which extends across the pores in the supporting matrix and contains a metal which is permeable to hydrogen but impermeable to the non-hydrogen components of the gas mixture. This may be provided by a method whereby the pores of the supporting matrix are at least partially filled or sealed off with the hydrogen-permeable metal, either by incorporating

a continuous foil or film of a hydrogen-permeable metal, such as palladium on the upstream side of the porous matrix or by incorporating a discontinuous series of hydrogen-permeable metal particles within the porous structure of the supporting matrix, the number of pores within the matrix sealed by the hydrogen-permeable metal particles being sufficient to provide a discontinuous passage to the non-hydrogen components of the gas mixture. The methods for fabricating a suitable separation unit to produce substantially pure hydrogen are numerous. In order to maintain the permeability of the hydrogen-permeable membrane at a higher level and thereby enable the use of high feed stock charging rates, it is essential to use a minimum quantity of hydrogen-permeable metal of which to construct the membrane, which quantity, however, must be sufficient to fill enough pores of the porous matrix to prevent the leakage of non-hydrogen components through the matrix. It appears that the transport of hydrogen through the hydrogen-permeable membrane essentially involves the dissolution of the hydrogen in an atomic state in the hydrogen-permeable metal and the subsequent diffusion of the dissolved atoms of hydrogen into the zone of reduced pressure on the downstream side of the membrane. When the path through which such diffusion must take place is long, by virtue of incorporating an excessive amount of hydrogen-permeable metal into the membrane, the concentration gradient of hydrogen through the metal will be small, resulting in a low rate of diffusion and considerable resistance to flow of hydrogen through the membrane.

The above factors involved in the preparation of the hydrogen-permeable membrane or cell are illustrated in Figure 1 of the accompanying drawing. The diagram of Figure 1 illustrates a porous matrix made up of a mass of variously sized compacted, sintered powdered steel particles, exemplified by the numeral 1 in Figure 1; this matrix contains discrete particles of the hydrogen-permeable metal selected from the metals of Group VIII of the Periodic Table, and preferably the metals of Series 4 and 6 of said Group VIII metals, or their hydrogen-permeable alloys distributed at random throughout the matrix, but filling a sufficient number of the pores between the compacted particles to eliminate free passageways for the non-hydrogen components of the gas mixture, preferably on the upstream side of the matrix. Such particles of hydrogen-permeable

metal are indicated by the numeral 2 in the illustration of the cut-away portion of the hydrogen-permeable membrane shown in Figure 1. It will be evident that if more than the required number of particles 2 are present in the porous matrix, undue resistance to the passage of hydrogen will be encountered because of the necessity of the hydrogen to dissolve in the metal before continuing its passage by diffusion through the porous structure. It is also evident that no more particles of the hydrogen-permeable metal are required in the matrix than will prevent a free passageway for the stream of non-hydrogen components on the upstream side of the membrane.

When referred to herein, the term "membrane" is intended to designate a continuous foil or film of the hydrogen-permeable metal or a discontinuous series of particles of the metal, providing a number of membrane elements distributed in the matrix support, either of which is impervious or forms a barrier to the passage of the non-hydrogen component or components of the feed stock gas mixture charged into the diffusion apparatus. Thus, the membrane may consist of a series of minute particles of only fractional micron thickness distributed at various levels in the porous matrix, and which, taken together, over the transverse area of the matrix present an impervious barrier to the non-permeable gaseous components. The term "porous" as utilized herein, indicates a structural condition in which spaced voids are dispersed throughout a solid mass and in sufficient number and continuity to permit fluid flow through the mass, while the term "permeable" is intended to characterize a condition which permits diffusion through the mechanism of dissolution, followed by displacement.

A number of methods may be utilized to form the hydrogen-permeable membrane comprising the diffusion apparatus of this invention. Thus, a relatively thick hydrogen-permeable foil, for example a foil of from 0.5 to about 20 microns in thickness may be placed upon the surface of a porous plate constituting the membrane support and the resulting combination placed in the diffusion cell as the hydrogen-permeable element of the apparatus. The thickness of the foil in this modification of the present apparatus should be only sufficient to withstand the pressure differential between the upstream and downstream sides of the foil without yielding to the pressure and forming a fissure or aperture through which the gaseous

mixture may flow. The required thickness of foil, will, in general, depend upon the size of the pores in the matrix and will also be determined by the desired rate of diffusion, which is inversely proportional to the thickness of the foil and varies directly with the pressure and temperature of the gaseous mixture impressed on the upstream surface of the foil. These are mutually dependent factors which can be determined readily for any particular system involved.

One of the preferred methods of preparing the hydrogen-permeable membrane comprises placing a thin foil on the surface of the matrix and subjecting the resulting combination to fluid pressure, such as to the pressure of the gaseous feed mixture at a pressure level at least as great as the pressure to be employed in the gas diffusion process and thereafter determining the purity of the hydrogen diffused through the membrane to the downstream side thereof. If the resulting hydrogen product is not of the desired purity, another layer of the hydrogen-permeable foil may be superimposed on the layer previously placed on the matrix and the procedure is then repeated until the continuity of the resulting membrane is sufficient to yield a diffused product of the desired purity. The thin foil from which the ultimate membrane is fabricated through the repeated applications of the foil to the porous plate may, for example, be a foil having a thickness substantially in the range of from 0.1 to 10 microns. When it is desired that the thickness of the membrane be increased gradually by the application of successive layers of foil to the upstream surface of the plate, the foil is preferably thin, such as a foil of 0.1 micron thickness. Instead of applying the foil by the application of fluid pressure, the foil may be pressed into the pores of the matrix by burnishing after each application. In general, it is preferred that this type of layered membrane be supported on its downstream side by a matrix, the pores of which are substantially of uniform size and are not greater than about 100 microns in diameter.

Figure 2 illustrates a typical arrangement of a type of apparatus utilizing a foil of the hydrogen-permeable metal as the membrane in the present gas diffusion process. In Figure 2, which is an isometric view of the internal portions of a typical gas diffusion cell, the portions are shown spaced from each other to more clearly

indicate the arrangement of the apparatus which in its assembled form provides a unit similar to that shown in Figure 3. In order to provide a working model

5 having a small number of component parts, a single hydrogen collection zone may be employed in combination with two hydrogen-permeable membranes and two membrane supports comprising the porous
10 matrices therefor; such apparatus provides for two upstream inlets, with the hydrogen product diffusing into an intermediate hydrogen-collecting zone. The permeable membrane on the two
15 upstream sides is indicated in Figure 2 by the numerals 3 and 4 and the adjacent porous matrices for these permeable membranes are indicated by the numerals 5 and 6, respectively. The hydrogen
20 collection zone which is placed between the downstream sides of the two opposing porous matrices 5 and 6 is indicated in Figure 2 by numeral 7. These may be clamped or bolted together into a unit.
25 Leakage of gas from the unit is prevented by sealing each of the pieces of the unit around their perimeters by means of gaskets, not shown, or by polishing the peripheral edges of the
30 pieces to provide an hermetically sealed union between the individual portions of the apparatus. Figure 3 illustrates one form of a typical gas diffusion apparatus embodying the elements of this
35 invention, above described, together with feed distribution zones 8 and 9 on the upstream sides of the hydrogen-permeable membrane on each end of the apparatus which also have their peripheral
40 edges sealed against the hydrogen-permeable membrane, as shown in Figure 3. The feed distribution zones 8 and 9 are connected to feed lines 10 and 11, respectively, which supply the respective
45 zones with the hydrogen-containing gas mixture to be separated. The feed gas mixture is preferably heated to an elevated temperature of at least 65°C. normally within the range of from 65° to
50 820°C., preferably to a temperature between 390° and 540°C., in order to increase the rate of hydrogen diffusion. The hydrogen component of the gas mixture, which, under the temperature and
55 pressure conditions maintained within the feed distribution zones, diffuses through hydrogen-permeable membranes 3' and 4', respectively, flows under the pressure existing within zones 8 and 9 through the porous membrane supports 12
60 and 13, respectively, into hydrogen-collection zone 14, the pressure differential between the feed-distribution zone and the hydrogen-collection zone being from 0.65 to 100 atmospheres,
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and preferably at least 1.4 atmospheres, with the pressure in the hydrogen-collection zone being maintained at not less than atmospheric pressure, in order
70 to obtain a positive flow of hydrogen from the upstream side of the hydrogen-permeable membrane into the hydrogen-collecting zone. As hydrogen accumulates in zone 14, it is withdrawn therefrom
75 through line 15 into storage or for other disposition. The flow of hydrogen-containing feed gas through one of the feed distribution zones 8 and 9 is preferably countercurrent to that through
80 the other feed distribution zone in order to take advantage of the concentration gradient effect inherent in gaseous diffusion; thus, the non-permeated gas outlets are desirably
85 located on the feed-collection zones on the side opposite to the feed gas inlets. This arrangement is illustrated in Figure 3 by pipes 16 and 17 which connect with the feed-distribution zones 8 and
90 9, respectively, through openings on the side opposite to the feed inlet openings 10 and 11, respectively.

Although the foil-type membrane constitutes one of the preferred forms of using the hydrogen-permeable metal in
95 the present gas diffusion cell, as illustrated in Figure 3, other types of preformed membranes may be utilized, as hereinafter indicated.

A simulated foil membrane which has
100 certain advantages over a continuous foil, above illustrated, more particularly in regard to ease of preparation and mechanical stability of the resulting membrane, may be formed by dusting
105 the surface of the porous matrix with the hydrogen-permeable metal in powdered form; a quantity of the powdered metal is used which reduces the perviousness of the resulting metal film to the non-hydrogen components of the gas mixture
110 to the desired level. Thus, palladium powder may be placed on the surface of the porous matrix and thereafter burnished or polished to form a more
115 continuous film over the pores of the supporting matrix. Another convenient method of placing a hydrogen-permeable metal film on the surface of the porous support comprises electroplating the
120 desired hydrogen-permeable metal or alloy on the upstream side of the porous support. Thus, palladium may be readily electroplated on the surface of
125 a sintered stainless steel powder plate by methods and procedures wellknown as such in the electroplating art. The electroplating process may be continued until the continuity of the hydrogen-permeable metal layer on the porous
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support has been developed to a degree sufficient to reduce the perviousness of the resulting membrane to the non-hydrogen components of the feed gas to the desired level. An alloy of the hydrogen-permeable metal, such as a platinum-silver alloy, may also be electroplated directly upon the porous plate.

Another method of applying a superficial layer or modified foil of the hydrogen-permeable metal on the upstream side of the porous matrix comprises permitting vapors of the metal to impinge on the surface of the matrix, usually by heating the metal in a high temperature electric arc (for example, electrodes fabricated from carbon) and allowing the vapors to rise to the flat surface of the matrix held above the metal being vaporized, as for example, above the electrodes. The vaporization may be effected under vacuum conditions, for example at 0.01 to 10 mm. Hg pressure, in order to increase the rate of vaporization at a lower temperature level. Suitable hydrogen-permeable metals utilizable in the application of the latter technique are palladium and palladium-silver alloys, among others. Still another method of placing a hydrogen-permeable metal film on the surface of a porous matrix comprises spraying the metal in molten condition onto the surface of the matrix maintained at a temperature below the melting point of the hydrogen-permeable metal, the process being generally known by the term "metallizing". Preferably, the sprayed layer or film of metal is built up by succeeding applications of thin layers, applied in the form of finely divided droplets, the size of the sprayed droplets decreasing as the velocity of gas through the metallizing equipment increases. This method may be applied more particularly in the forming of a film of hydrogen-permeable metal or alloy of relatively low melting point.

Another method of fabricating the supported hydrogen-diffusion membrane comprises incorporating the hydrogen-permeable metal into the porous support by impregnating the porous matrix with a decomposable salt of a hydrogen-permeable metal (for example, palladium nitrate) or with a mixture of the decomposable salts of a hydrogen-permeable metal and an alloying metal thereof, and thereafter reducing the salt or salts contained within the porous support to produce a metallic deposit of the hydrogen-permeable metal or alloy within the matrix of the porous support. The

impregnation may be applied advantageously to that side of the porous matrix which will be used as the upstream side or high pressure side in the gas diffusion cell. Salt solutions of various concentrations may be employed to control the perviousness of the resulting membrane to the non-hydrogen components of the feed mixture, the perviousness decreasing as the concentration of salts in the impregnating solution increases. It is expedient to gradually increase the continuity of the hydrogen-permeable metal in the membrane up to the extent desired for the required purity of product to thereby determine the minimum quantity of hydrogen-permeable metal for maximum purity of the hydrogen product. This procedure comprises impregnating the porous matrix with a dilute solution of the hydrogen-permeable metal salt, thereafter decomposing the salt, determining the purity of hydrogen obtained by using the resultant membrane and, if the hydrogen is not sufficiently pure, repeating the series of steps of impregnating, decomposing and testing until a product of the desired purity is obtained. A suitable class of salts for this purpose are the nitrates from which the hydrogen-permeable metal may be readily formed by reduction with hydrogen or by precipitation with hydrogen sulfide, followed by treatment of the metal sulfide with air or oxygen at elevated temperature.

Still another method for incorporating the hydrogen-permeable metal membrane into the matrix of the porous support comprises mixing the hydrogen-permeable metal in powdered form with the matrix-forming material before the latter is compacted and sintered, thereby preparing the matrix and the membrane in the same operation. This method is particularly suitable when the supporting matrix is made of sintered stainless steel powder. In this method, the perviousness of the resulting membrane, in combination with the desired porous matrix is directly proportional to the amount of powdered hydrogen-permeable metal incorporated into the matrix-forming material and may also be controlled by varying the mechanical and thermal treatment of the formed matrix membrane combination to provide a membrane of the desired perviousness. Thus, the perviousness of the combined matrix and membrane may be reduced by sintering the metal powder at a higher temperature, thereby at least partially sealing the porous structure of the matrix while not

substantially affecting the permeability of the membrane to hydrogen diffusion.

It is evident that various modifications of the illustrated apparatus may be employed in carrying out the method of this invention. Thus, for example, two or more of the hydrogen diffusion cells may be interconnected in series, with or without intermediate compressors at one or more intermediate points in the series of the cells in order to produce a hydrogen product of greater purity by subjecting the diffusate from one cell to additional treatment in succeeding cells or in order to increase the recovery of hydrogen from a given gas mixture by subjecting the non-diffused effluent to additional hydrogen diffusion treatments.

The method of separation provided herein may be adapted to many types of feed stocks, including corrosive mixtures as well as substantially inert mixtures of hydrogen-containing gases. Thus, hydrogen may be recovered from mixtures containing low molecular weight hydrocarbons such as methane, ethane and ethylene, for example, the non-condensable gas mixtures formed in thermal or catalytic cracking of petroleum oils. Other feed stocks for the present method are gas streams of low hydrogen concentration, such as the lean gas effluent of an absorber operated in conjunction with a catalytic cracking process, which may contain as low as a fractional mol percent of hydrogen. Another typical charging stock which may be supplied to the present process for the purpose of purifying the hydrogen therein is a hydrogen-nitrogen mixture obtained by autothermic reaction of a methane-steam-air mixture, followed by absorption of the carbon dioxide component of the resulting gaseous mixture in an aqueous caustic solution. The hydrogen-nitrogen mixture may contain any concentration of hydrogen. Still another use of the present method is the increasing of the hydrogen concentration in the recycle hydrogen stream of a hydrocarbon reforming process. The hydrogen-containing recycle gas mixture recovered from the downstream side of the reforming reaction is generally contaminated with such gases as hydrogen sulfide and methane and the recycled gas is preferably purified of such contaminants prior to being recycled to the reforming reaction zone, and the present process provides a convenient means of effecting such purification.

This invention is further illustrated by the following examples which indicate typical embodiments of hydrogen

diffusion apparatus and method of a hydrogen diffusion, all in accordance with the present invention and which also indicate the character of the results obtainable thereby.

EXAMPLE I

A hydrogen diffusion cell in simplified form is fabricated in accordance with the following procedure. A porous plate measuring 30.5 cm x 30.5 cm x 2.54 cm in dimension is utilized as a supporting porous matrix, the plate consisting of sintered particles of stainless steel powder (steel containing 18% chromium and 8% nickel) molded into a structurally rigid form by heating and compressing the stainless steel powder of 10 microns average particle diameter at or near the melting point of the stainless steel. The plate is fitted into a housing which hermetically seals the peripheral edge of the plate against the walls of the housing, the plate dividing the housing approximately through its mid-section, thereby providing an enclosure on each side of the plate sealed on each side against the leakage of gases from the enclosure on one side of the plate into the enclosure on the other side of the plate. The apparatus is so designed and fabricated that different plates of 2.54 cm thickness may be substituted into the mid-section of the housing for test purposes. In the following example, the plate of sintered stainless steel particles which weighs approximately 8.57 kg. has pore diameters which vary in diameter from about 2 microns to about 10 microns. When placed in the gas diffusion cell the plate allows approximately 2,832 liters per minute of a mixture of 25% hydrogen and 75% nitrogen to pass through the plate per minute at an upstream pressure of 0.68 atmospheres.

The porous stainless steel plate indicated above is thereafter soaked in a 0.9% solution of palladium dinitrate placed in a shallow pan, the solution being maintained at a level of 12.7 mm depth as the solution enters the porous structure of the upstream side of the sintered stainless steel plate. The plate containing the solution of palladium dinitrate is thereafter slowly dried in an oven at 110°C. for ten hours, followed by heating the impregnated plate in an oven maintained at 900°C. for an additional 12 hours to decompose the palladium dinitrate salt to metallic palladium. The weight of the porous plate after the above treatment increased an additional 4.87 grams. When tested in the gas diffusion cell,

this plate permits the passage of 1,415 liters gas per minute from a mixture of 25% of hydrogen and 75% nitrogen at an upstream pressure of 0.68 atmospheres and at a temperature of 115°C, and the diffused gas which is withdrawn from the chamber on the downstream side of the sintered plate is enriched in hydrogen as it contains 45% by volume of hydrogen and 55% by volume of nitrogen.

The plate is thereafter removed from the gas diffusion apparatus and placed in a pan containing a 0.045% aqueous solution of palladium dinitrate to a depth of 12.7 mm from the top edge of the sintered metal plate. After soaking in the latter solution for 3 hours the plate is again dried and then heated for 12 hours at 900°C. and thereafter is placed again into the gas diffusion cell for determining the rate of diffusion and the concentration of hydrogen in the diffused gas. At a pressure of 0.68 atmospheres, and with the gas mixture at 115°C. the plate permits the passage of 1160 liters per minute of gas enriched in hydrogen, the collected gas containing 93% by volume of hydrogen and 7% by volume of nitrogen.

The plate as prepared by the second impregnation of palladium metal is again placed in the shallow pan containing an aqueous solution of 0.045% by weight of palladium dinitrate for three hours, followed by decomposition of the impregnated palladium nitrate at 900°C. for ten hours. The resulting plate placed in the gas diffusion cell and tested with the same initial mixture containing 75% nitrogen and 25% hydrogen at a pressure of 0.68 atmospheres and a temperature of 115°C. on the upstream side permits the passage of 595 liters per minute of a hydrogen concentrate containing 99.5% hydrogen and 0.5% nitrogen. Utilizing a pressure of 6.8 atmospheres at 115°C. on the upstream side of the sintered plate containing the palladium membrane, 3,490 liters per minute of hydrogen concentrate are collected in the diffused gas collection compartment and this concentrate contains 98.4% by volume of hydrogen and 1.6% by volume of nitrogen. At 6.8 atmospheres pressure and 300°C., 11,553 liters per minute of hydrogen concentrate containing 97.5% by volume of hydrogen pass through the cell.

EXAMPLE II

A sintered plate of powdered stainless steel was used in practically the same manner as described in the above Example I, except that in each of the three successive impregnations the total salt in the aqueous impregnating solution contained 50 mol % of palladium

dinitrate and 50 mol % of silver nitrate and this aqueous solution was utilized to prepare the hydrogen-permeable membrane. Following each impregnation with the above solutions of mixed palladium and silver nitrates, the impregnated plate was dried and the salts contained in the plate were decomposed at a temperature of 1000°C. in order to form an alloy of the silver-palladium metal in the porous plate. At an upstream pressure of 6.8 atmospheres and a temperature of 115°C., a mixture of 75% nitrogen and 25% hydrogen permits the passage of 2,795 liters per minute of a gas diffusate containing 99.5% hydrogen and 0.5% nitrogen.

EXAMPLE III

A palladium foil of 2.03 micron thickness was supported by a sintered plate of compressed stainless steel powder, the surface of which had been polished and cleaned. This porous plate had been produced in the same manner as indicated in Example I, and the cleaning of the polished plate was effected with an etching solution containing 15% HNO₃ and 5% HF until the porosity was fully restored on the polished side, this being determined by the flow of air through the porous plate. The resultant membrane supported on the upstream side of the porous plate was found to remain completely free from rupture at a temperature of 4550 and a pressure difference of more than 28 atmospheres between the upstream side of the membrane and the downstream side of the porous plate.

This supported membrane was used in a single diffusion plate cell for purifying a stream of hydrogen contaminated by 0.7% nitrogen. The cell was operated at a temperature of 454°C. At an upstream pressure of 27.2 atmospheres with the downstream portion of the diffusion cell at atmospheric pressure, pure hydrogen was diffused into the downstream portion of the cell at the rate of 9.15 standard liters (measured at 0°C. and 760 mm Hg) per hour per cm² of the supported palladium membrane. Pure hydrogen was obtained as diffusate from the same contaminated hydrogen in the same diffusion cell at the rate of 7.02 standard liters per hour per cm² of the membrane when operating the diffusion cell at a temperature of 454°C. with an upstream pressure of 47.5 atmospheres and a downstream pressure of 20.4 atmospheres.

EXAMPLE IV

A diffusion cell containing the same supported palladium membrane as described in Example III was used for separating hydrogen from a mixture

consisting of hydrogen and methane in the proportion of 2 mols hydrogen to 1 mol methane. The diffusion cell was operated at a temperature of 454°C. with an upstream pressure of 47.6 atmospheres and a downstream pressure of 20.4 atmospheres. Undiffused gas was continuously withdrawn from the upstream portion of the cell at a point opposite to and remote from the point of the continuous introduction of the mixture into the upstream portion of the cell. The rate of withdrawal of undiffused gas was varied over the range of from 3.1 to 8.4 volumes per volume of diffusate. A diffusate consisting of pure hydrogen was obtained from the downstream portion of the cell at the rate of 0.67 standard liters per hour per cm² of the supported membrane when withdrawing undiffused gas at the rate of 3.1 volumes per volume of diffusate, and a diffusate consisting of pure hydrogen was obtained at the rate of 1.68 standard liters per hour per cm² of the supported membrane when withdrawing gas from the upstream portion of the cell at the rate of 8.4 volumes per volume of diffusate.

It is to be noted that in both this Example and Example III, the continuous membrane of palladium was found to have an appreciably greater thickness than is needed for use without any danger of breaking at the conditions of elevated temperature and pressure described when it is directly supported on the rigid porous matrix of compressed sintered metal particles. By applying a superficial layer of palladium on the upstream side of such porous matrix by one of the above described preferred methods, for example by electroplating or vapor-plating, a thinner continuous membrane of the hydrogen-permeable metal can be deposited on the porous matrix with the result that, at otherwise equal conditions of elevated temperatures and pressures and without rupturing the membrane, specific hydrogen diffusion rates can be obtained which are up to about ten times greater than the specific diffusion rates obtained in the above Examples III and IV.

WHAT WE CLAIM IS:-

1. A method of producing a gas stream of increased hydrogen concentration from a hydrogen-containing mixture of gases which comprises passing said mixture at an elevated pressure and temperature through a diffusion zone separated into an upstream portion and a downstream portion by a membrane as hereinbefore defined comprising a hydrogen-permeable metal of Group VIII of the Periodic Table, said membrane being supported

against the upstream pressure by a rigid porous matrix comprising compressed sintered steel particles, and collecting a gas stream of higher hydrogen concentration than that of said mixture on the downstream side of said matrix while a gas stream of lower hydrogen concentration than that of said mixture is collected on the upstream side of said membrane.

2. Method as claimed in claim 1 wherein pure hydrogen is diffused from the mixture through a membrane consisting of a metal selected from Group VIII of the Periodic Table and the hydrogen-permeable alloys of said Group VIII metal, said membrane being supported on its downstream side by a rigid porous matrix produced from stainless steel particles of from 1 to 100 micron particle size.

3. Method as claimed in claim 2 wherein hydrogen is diffused from the mixture through a membrane supported on its downstream side by a matrix having pores of not more than 100 micron diameter.

4. Method as claimed in any of the claims 1 to 3 wherein the mixture is supplied to the upstream portion of the diffusion zone at a temperature of at least 650°C., a difference of from 0.65 to 100 atmospheres is maintained between the pressures in the upstream portion and the downstream portion of said zone, and the pressure in said downstream portion is maintained at not less than atmospheric pressure.

5. Method as claimed in claim 4 wherein the mixture is supplied to the upstream portion of the diffusion zone at a temperature in the range of from 390 to 540°C. and a difference of at least 1.4 atmospheres is maintained between the upstream and downstream pressures.

6. Method as claimed in any of the claims 1 to 5 wherein hydrogen is diffused from the mixture through a continuous membrane consisting of palladium or a hydrogen-permeable alloy of palladium supported on the upstream side of a porous matrix composed of compressed sintered stainless steel powder.

7. The method of producing a gas stream of increased hydrogen concentration from a hydrogen-containing mixture of gases substantially as described.

8. Apparatus for producing a gas stream of increased hydrogen concentration from a hydrogen-containing mixture of gases, which comprises in combination a housing capable of confining a mixture of gases under pressure and at elevated temperature, a structurally rigid porous matrix composed

substantially of compressed sintered steel particles and sealed into the sides of said housing and between the ends thereof, a gas inlet to and a gas outlet from said housing on one side of said matrix, said inlet and outlet being spaced from each other, a separate gas outlet from said housing on the other side of said matrix, and a membrane as hereinbefore defined which extends across the entire free area within said housing and is supported by said matrix, said membrane comprising a metal selected from Group VIII of the Periodic Table and the hydrogen-permeable alloys of said Group VIII metal.

9. Apparatus as claimed in claim 8 wherein the matrix consists of compressed sintered stainless steel particles and has pores of not more than 100 micron diameter, and said membrane is supported on the upstream side of said porous matrix.

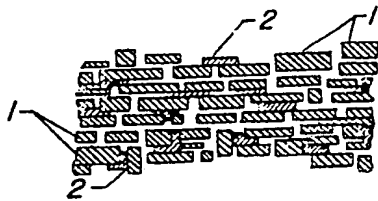
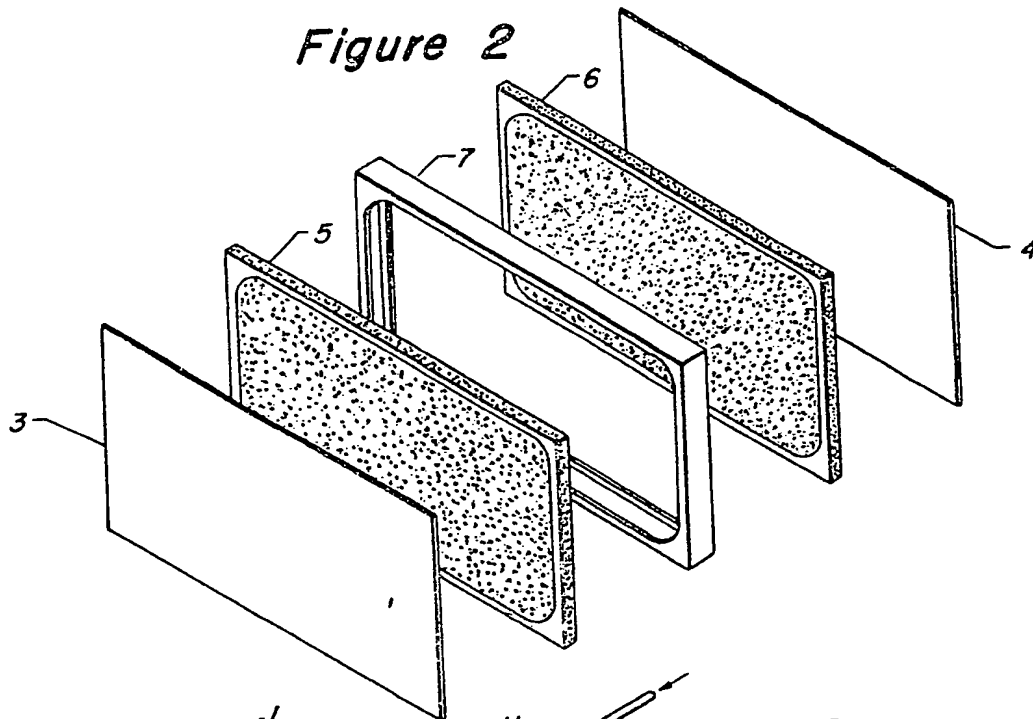
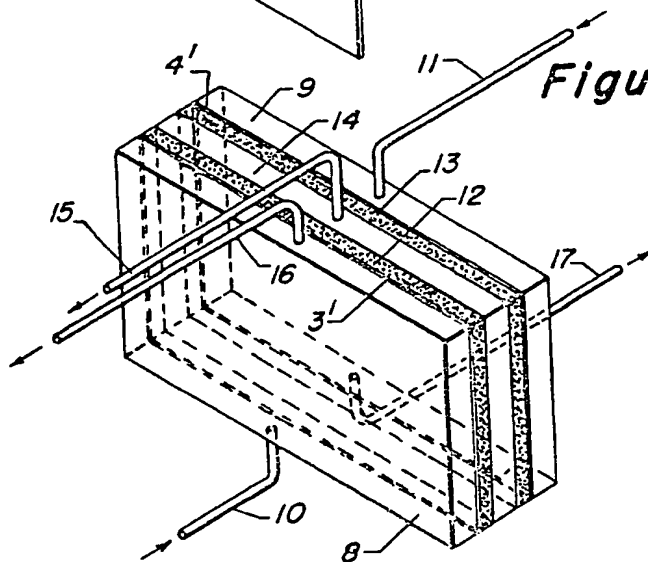
10. Apparatus as claimed in claim 9 wherein the porous matrix consists of compressed sintered stainless steel particles of from 1 to 100 micron particle size and supports a continuous membrane consisting of palladium.

11. The apparatus for producing a gas stream of increased hydrogen concentration from a hydrogen-containing mixture of gases as claimed in claim 8 substantially as described with reference to the drawings.

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**Figure 1****Figure 2****Figure 3**